



Photocatalytic reduction of platinum(II and IV) from their chloro complexes in a titanium dioxide suspension in the absence of an organic sacrificial reducing agent

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ABSTRACT

The thermodynamics and surface chemistry affecting the photocatalytic reduction of chloro aqua platinum(II) and platinum(IV) complexes as means of platinum recovery from solution are communicated. The photocatalytic reduction rate trends of the cationic, neutral and anionic chloro complexes under acidic conditions in the TiO_2 aqueous suspension in air equilibrated solutions, oxygen as well as nitrogen-purged solutions are discussed. Speciation of platinum is used to explain the observed photocatalytic reduction processes and trends. The rate of reduction was found to be highest for the cationic species $[\text{Pt}(\text{H}_2\text{O})_4]^{2+}$ and $[\text{PtCl}(\text{H}_2\text{O})_3]^+$ in line with thermodynamic predictions whilst no reduction was observed for the tetrachlorinated $[\text{PtCl}_4]^{2-}$ complex in each of the three atmospheres. The role of water in the coordination sphere of the platinum(II) chloro aqua complexes is discussed and a comparison is made with the photocatalytic reduction of platinum(IV) from its hexa-chloro compounds without any water in their coordination spheres.

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1. Introduction

Platinum group metals (PGMs), due to their noble characteristics and catalytic activity find specific application in the chemical industry. They are increasingly used in applications such as autocatalysts, jewellery and electronics. The anionic chloro complexes of these metals are usually exploited during the metallurgical recovery, separation and purification from primary sources. The recovery process includes ligand substitution kinetics, redox potentials as well as ion exchange reactions [1]. With increased awareness of their scarcity and potential water pollution during their recovery, interest has increased in their recovery from waste water streams using environmentally benign processes. One such process is photocatalytic reduction and many articles have been published for the recovery of these metals from solutions employing photocatalysis [2–4]. However, only one publication dealt with the photocatalytic reduction rate trends of a platinum group metal namely, palladium as a function of chloride concentration in the absence of an added sacrificial reducing agent (SRA) [5]. In that communication, the photocatalytic reduction rate trend was observed to have the following decreasing order: $\text{PdCl}_2(\text{H}_2\text{O})_2 > [\text{PdCl}(\text{H}_2\text{O})_3]^+ > [\text{Pd}(\text{H}_2\text{O})_4]^{2+} > [\text{PdCl}_3(\text{H}_2\text{O})]^- > [\text{PdCl}_4]^{2-}$, with $[\text{PdCl}_4]^{2-}$ showing resistance to photocatalytic reduction in the

absence of an added SRA. It was postulated that photocatalytic oxidation of the coordinated water molecules impacts on the rate of photocatalytic reduction. For those complexes for which the ratio $\text{H}_2\text{O}:\text{Cl}^-$ is greater than 50%, the oxidation of coordinated ‘in-sphere’ water molecules is working against an expected increase in the rate of reduction as predicted by the complexes’ standard reduction potentials. Interplay between thermodynamics and adsorption/interaction of the palladium species on the photocatalyst surface was clearly shown to be at work in that system. The parameters affecting the kinetics and mechanisms of photocatalysis have been reported elsewhere [6–9]. The photocatalytic reduction and deposition of metallic platinum onto titanium dioxide particles in aqueous suspension with different complex solutions (chloroplatinic acid, sodium chloroplatinate, hexahydroxyplatonic acid, and platinum-dinitrodiamine) in the absence of an added SRA has been carried out before [10]. A number of factors governing the photocatalytic reduction and deposition of platinum were investigated showing that the deposition can occur from various platinum complexes. The exhaustion of a solution was shown to reach 1 ppm and the deposition was not limited by the saturation of the semiconductor grains by the platinum particles. In that study it was concluded that the results could lead to a photodeposition method as a means of noble metal recovery. In another study [11], the kinetics and mechanism of platinum photocatalytic reduction and deposition was carried out using platinum hexachloride solutions. The best results were obtained in a solution of low pH, low light intensity, high ionic strength,

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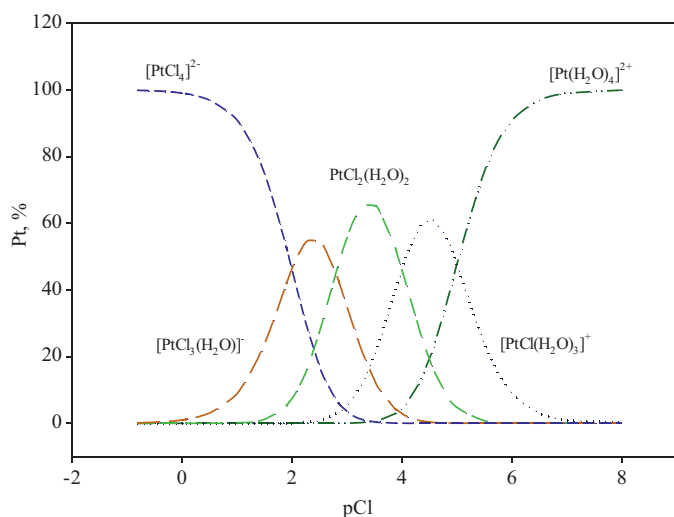


Fig. 1. Distribution of $[\text{PtCl}_n(\text{H}_2\text{O})_{4-n}]^{2-n}$ species as a function of pCl ($-\log[\text{Cl}^-]$).

low oxygen content and at temperatures higher than ambient. The initial metal salt concentration was found to be insignificant and therefore deposition could be carried out from dilute solutions. Here, we report the differences in the removal rates of some of the chloro aqua complexes of platinum(II) from solution in the absence of an added organic SRA, at constant pH, ionic strength, temperature and light intensity. The effect of dissolved oxygen is explored and compared to the photocatalytic reduction of hexachloroplatinic acid (H_2PtCl_6) and potassium chloroplatinate (K_2PtCl_6). The speciation of platinum(II) with chloride is well documented [12–14] and using these data, solutions containing the maximum of each species, that is; $[\text{Pt}(\text{H}_2\text{O})_4]^{2+}$, $[\text{PtCl}(\text{H}_2\text{O})_3]^+$, $\text{PtCl}_2(\text{H}_2\text{O})_2$, $[\text{PtCl}_3(\text{H}_2\text{O})]^-$ and $[\text{PtCl}_4]^{2-}$ were prepared and subjected to photocatalytic reduction.

2. Experimental

2.1. Reagents and stock solution

Platinum(II) chloride (99.99%, Ultraspec) stock solution was prepared by dissolving 5 g PtCl_2 in 3 M HClO_4 (Saarchem Pty Ltd, 70%). Since the salt is almost insoluble in water, it was added to the acidic solution and stirred for 2 h. Undissolved salt was filtered and the filtrate concentration of Pt in the stock solution was determined by ICP-OES and used to prepare individual neutral and anionic chloro aqua complexes of platinum(II). The cationic chloro aqua complexes of Pt(II) were prepared from a $\text{Pt}(\text{NO}_3)_2$ solution containing 10% platinum (Heraeus Chemicals). Urbansky [15], states that the NO_3^- anion's low charge density reduces its affinity for cations, hence it can easily be substituted by other ligands like Cl^- and H_2O . NaCl (99.98%, Sigma Aldrich) was used to adjust the chloride concentration as per the platinum(II) chloride distribution diagram (Fig. 1), while $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ (Sigma Aldrich) was used to adjust the ionic strength of each solution. Deionised water from a Millipore Milli-Q system was used to prepare all solutions. Evonik-Degussa P25 TiO_2 , with a surface area $50.5 \text{ m}^2 \text{ g}^{-1}$, was employed as photocatalyst, with the amount of TiO_2 in suspension being 2 g dm^{-3} . A stock solution of K_2PtCl_6 from Sigma Aldrich was prepared by dissolution of the salt in 1 M HClO_4 . H_2PtCl_6 was prepared by dissolving 1 g of platinum sponge (99.999%, Ultraspec) in 40 mL 3:1 (v/v) mixture of HCl and HNO_3 . The nitrates were driven off by mild heating and the resultant dark yellow jelly like product was diluted with 1 M HClO_4 and kept as stock solution. The starting

Table 1

Overall formation constants ($\log \beta_n$) for the $[\text{PtCl}_n(\text{H}_2\text{O})_{4-n}]^{2-n}$ ($n = 1-4$) system.

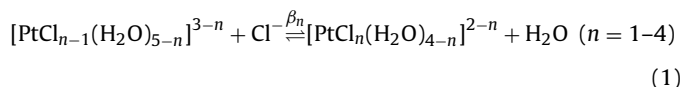
n	$[\text{PtCl}_n(\text{H}_2\text{O})_{4-n}]^{2-n}$	$\log \beta_n$
1	$[\text{PtCl}(\text{H}_2\text{O})_3]^+$	5.00
2	$\text{PtCl}_2(\text{H}_2\text{O})_2$	9.00
3	$[\text{PtCl}_3(\text{H}_2\text{O})]^-$	11.80
4	$[\text{PtCl}_4]^{2-}$	13.80

platinum concentration in a 500 mL reaction solution was 50 ppm or $2.56 \times 10^{-4} \text{ M}$.

2.2. Chloro aqua complexes of Pt(II)

The formation constants (Table 1) of the respective complexes of the $[\text{PtCl}_n(\text{H}_2\text{O})_{4-n}]^{2-n}$ ($n = 1-4$) system, were sourced from literature [14].

The distribution (Fig. 1) of the Pt(II)-chloride complexes as a function of pCl was calculated from these formation constants for the following complexation reactions:



Each solution, to be illuminated, was prepared at the specific pCl value coinciding with the maximum of each $[\text{PtCl}_n(\text{H}_2\text{O})_{4-n}]^{2-n}$ species ($n = 0-4$) indicated by the values in bold in Table 2. The correct chloride concentration for each solution was obtained by the addition of NaCl (Tables 2 and 3). In order to obtain a constant ionic strength of 1 mol dm^{-3} , for all illuminated solutions, the balance of the solution was made up with $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ (Table 3). The acid concentration (HClO_4), constant for each illuminated solution, was such that the pH of each solution was approximately 1.

With the distribution of the Pt(II)-chloride complexes known, the photocatalytic reduction trends of these complexes were subsequently investigated at those Cl^- concentrations that coincide with the maximum of each species. As for the K_2PtCl_6 and H_2PtCl_6 reaction solutions the pH was also maintained at 1 and no attempt was made to adjust the ionic strength for comparison purposes with the $[\text{PtCl}_4]^{2-}$ complex for which no $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ was added.

2.3. Experimental apparatus

The closed-loop experimental setup used in this investigation was similar to the one employed for our investigation of the photocatalytic reduction of the palladium(II) chloride system [5]. The source of UV light was a blacklight fluorescent lamp (15 W), which emits light between 300 and 425 nm with a peak at 350 nm, which is below 383 nm (Evonik-Degussa P25 bandgap) and is therefore efficient for charge separation. The reaction atmosphere was medical grade oxygen, ambient air or analytic grade nitrogen at 25°C . In case of oxygen and nitrogen the solution in the reservoir was purged for 30 min prior to illumination while stirring to allow for maximum adsorption of the reactants to the photocatalyst and continuously thereafter for the duration of the experiment. During a run of 150 min, 10 mL samples were taken from the reservoir at 15 min intervals and filtered for analysis by means of inductively coupled plasma (ICP) emission spectroscopy employing a Thermo iCAP 6300 instrument.

3. Results and discussion

3.1. Thermodynamic analysis

The photocatalytic reduction of Pt(II) is thermodynamically favourable in acidic conditions [16–18]. However, another

Table 2Speciation of the $[\text{PtCl}_n(\text{H}_2\text{O})_{4-n}]^{2-n}$ -system ($n=0-4$) as a function of pCl at 25 °C, constant pH and ionic strength 1 respectively.

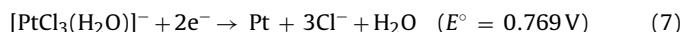
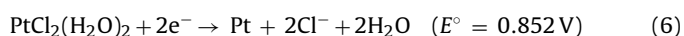
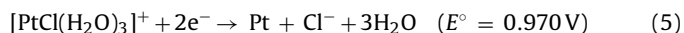
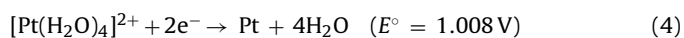
pCl	$[\text{Cl}^-]$ (M)	%				
		$[\text{Pt}(\text{H}_2\text{O})_4]^{2+}$	$[\text{PtCl}(\text{H}_2\text{O})_3]^+$	$[\text{PtCl}_2(\text{H}_2\text{O})_2]$	$[\text{PtCl}_3(\text{H}_2\text{O})]^-$	$[\text{PtCl}_4]^{2-}$
0.05	8.89×10^{-1}	0.000	0.000	0.002	1.112	98.886
2.39	4.06×10^{-3}	0.001	0.531	21.596	55.371	22.500
3.41	4.00×10^{-4}	0.435	16.925	65.847	16.164	0.629
4.51	3.08×10^{-5}	19.834	61.025	18.776	0.365	0.001
11.00	0.00	100.000	0.000	0.000	0.000	0.000

consideration is the surface of TiO_2 photocatalysts which has a point of zero charge value around pH 7 as reported by a number of authors [19–21]. Below this pH, the TiO_2 surface has a net positive charge and above this pH, it has a negative charge. Therefore, the anionic species of platinum(II) ions should be deposited well in the acidic pH range whereas the cationic species in the alkaline pH range. When the standard reduction potentials of these complexes are considered, one sees an agreement between thermodynamics and kinetics (Eqs. (4)–(8) and Fig. 2) unlike the case with the chloro aqua palladium(II) complexes (5). Considering for a moment the reduction of the four coordinated species to the zero valency state, the following applies:

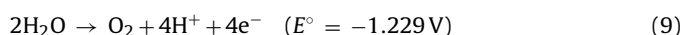


$$E = E^\circ - \left(\frac{0.0591}{2} \right) \log \left\{ \frac{[\text{Cl}^-]^4}{[[\text{PtCl}_4]^{2-}]} \right\} \quad (3)$$

From Eq. (3) it follows that a higher Cl^- -concentration would give rise to a lower value for E , which implies that Pt(II) will be increasingly more difficult to reduce. Applying the Nernst equation to calculate the E° -values from the log β -values obtained, for the individual half-reactions (Eqs. (4)–(8)), it is seen that there is a decrease in the E° -values with higher coordination of Cl^- .



The calculated E° -value for the reduction of $[\text{PtCl}_4]^{2-}$ to Pt^0 (Eq. (8)) compares well with the value stated in literature of 0.73 V [16]. Thermodynamically, however, these complexes are stable in water and are not reduced by H_2O under normal conditions (in the absence of a catalyst) as the oxidation of water in acidic media occurs at -1.229 V under standard conditions (Eq. (9)).



From the calculated standard reduction potentials (Eqs. (4)–(8)) one would expect $[\text{PtCl}_4]^{2-}$ to be the least prone to reduction while $[\text{Pt}(\text{H}_2\text{O})_4]^{2+}$ would be the easiest to reduce, i.e. the

expected order of the decreasing rate of reduction would be as follows: $[\text{Pt}(\text{H}_2\text{O})_4]^{2+} > [\text{PtCl}(\text{H}_2\text{O})_3]^+ > \text{PtCl}_2(\text{H}_2\text{O})_2 > [\text{PtCl}_3(\text{H}_2\text{O})]^- > [\text{PtCl}_4]^{2-}$. Another important point however, is the influence of dissolved oxygen on the photocatalytic reduction rates of platinum(II) chloro aqua complexes. For this study, experiments were carried out in air, pure oxygen and nitrogen-purged suspensions and the trends of the photocatalytic reduction of these complexes are discussed in the following sections.

3.2. Photocatalytic reduction of Pt(II) chloro aqua complexes in oxygen, air and nitrogen

Fig. 2 shows the effect of the three atmospheres on the photocatalytic reduction of Pt(II) chloro aqua complexes. From the figure and the initial rates of reduction (Fig. 3) it is clear that oxygen reduction is in competition with the reduction of platinum(II) chloro aqua complexes as it slows down the complexes' reduction rates. Oxygen reduction ($E^\circ = 1.229 \text{ V}$) is thermodynamically more favourable than the reduction of all the complexes. In the presence of a saturated amount of O_2 there is clear separation in the kinetics of $[\text{Pt}(\text{H}_2\text{O})_4]^{2+}$ and $[\text{PtCl}(\text{H}_2\text{O})_3]^+$ reduction, which can be attributed to the differences in the adsorption of these complexes onto the titanium dioxide particles in the presence of pure oxygen. The observed trend is: $[\text{Pt}(\text{H}_2\text{O})_4]^{2+} > [\text{PtCl}(\text{H}_2\text{O})_3]^+ > \text{PtCl}_2(\text{H}_2\text{O})_2 > [\text{PtCl}_3(\text{H}_2\text{O})]^- = [\text{PtCl}_4]^{2-}$. The high reduction potentials for $[\text{Pt}(\text{H}_2\text{O})_4]^{2+}$, $[\text{PtCl}(\text{H}_2\text{O})_3]^+$ and $\text{PtCl}_2(\text{H}_2\text{O})_2$ (1.118 V, 0.970 V and 0.852 V) compared to 1.229 V for O_2 reduction slightly offsets the negative effect of oxygen thus significant reduction is observed. This is not so for $[\text{PtCl}_3(\text{H}_2\text{O})]^-$ and $[\text{PtCl}_4]^{2-}$ with lower reduction potentials of 0.769 V and 0.710 V respectively, which cannot compete with oxygen reduction at pH 1.

In air the $[\text{Pt}(\text{H}_2\text{O})_4]^{2+}$ and $[\text{PtCl}(\text{H}_2\text{O})_3]^+$ complexes again exhibit the highest reduction kinetics compared to the other three complexes. This is not unexpected since thermodynamically these two complexes have the highest reduction potentials. The exhibition of the same kinetics can be explained by speciation where the amount of chloride added for the preparation of the $[\text{PtCl}(\text{H}_2\text{O})_3]^+$ complex is negligible at $3.08 \times 10^{-5} \text{ M}$ (Table 2) although thermodynamically $[\text{Pt}(\text{H}_2\text{O})_4]^{2+}$ should be easier to reduce than $[\text{PtCl}(\text{H}_2\text{O})_3]^+$. The initial rates of reaction of these complexes in air are shown in Fig. 3. The observed order of reduction in air (the mean of three repeats) depicted in Fig. 2 is: $[\text{Pt}(\text{H}_2\text{O})_4]^{2+} = [\text{PtCl}(\text{H}_2\text{O})_3]^+ > \text{PtCl}_2(\text{H}_2\text{O})_2 > [\text{PtCl}_3(\text{H}_2\text{O})]^- > [\text{PtCl}_4]^{2-}$ (compare with palladium in Ref. [5]). The individual Pt(II)-solutions, prepared

Table 3Adjustment of the ionic strength (I) to 1 M for each solution. Pt(II) concentration was 50 ppm.

Pt(II) species	Pt^{2+} (mol l ⁻¹)	NO_3^- (mol l ⁻¹)	HClO_4 (mol l ⁻¹)	NaCl (mol l ⁻¹)	NaClO_4 (mol l ⁻¹)	I
$[\text{Pt}(\text{H}_2\text{O})_4]^{2+}$	2.56×10^{-4}	5.13×10^{-4}	0.100	0.000	0.900	1
$[\text{PtCl}(\text{H}_2\text{O})_3]^+$	2.56×10^{-4}	5.13×10^{-4}	0.100	3.08×10^{-5}	0.900	1
$\text{PtCl}_2(\text{H}_2\text{O})_2$	2.56×10^{-4}	–	0.110	0.000 ^a	0.890	1
$[\text{PtCl}_3(\text{H}_2\text{O})]^-$	2.56×10^{-4}	–	0.110	4.10×10^{-4}	0.885	1
$[\text{PtCl}_4]^{2-}$	2.56×10^{-4}	–	0.110	8.89×10^{-1}	0.000	1

–, prepared from PtCl_2 salt.^a The chloride concentration from stock solution was such that no NaCl was needed.

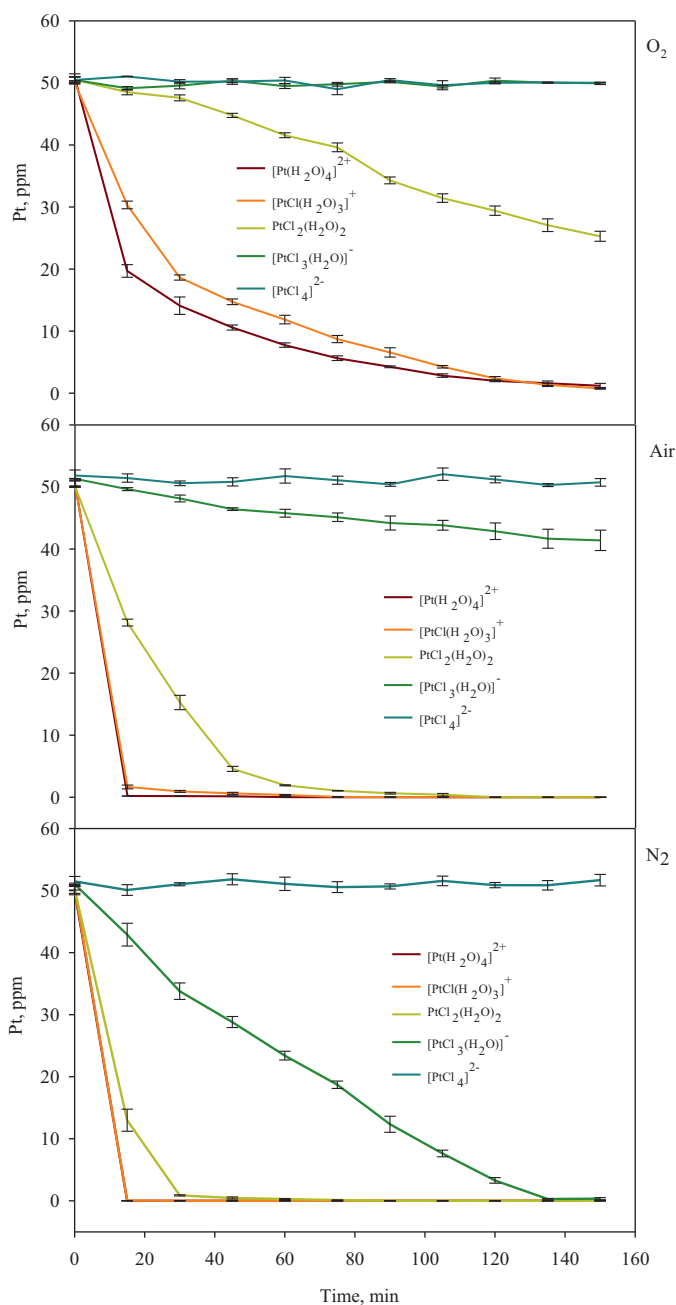


Fig. 2. Photocatalytic reduction trends of the $[\text{PtCl}_n(\text{H}_2\text{O})_{4-n}]^{2-n}$ -system ($n=0-4$) in the absence of an added SRA in oxygen, air and nitrogen.

at the chloride concentrations coinciding with the maximum of each species, contains Pt(II)-complexes in equilibrium with one another. The photocatalytic reduction behaviour of Pt(II) at those chloride-concentrations is therefore related to all Pt(II)-complexes present at that specific chloride-concentration. However, at those points where the individual solutions were prepared the complex present in greatest abundance dominates its nearest rival by a fair amount. From the speciation (Table 2) it is clear that $\text{PtCl}_2(\text{H}_2\text{O})_2$ dominates its nearest rival by $\sim 49\%$, $\sim 34\%$ in the case of $[\text{PtCl}_3(\text{H}_2\text{O})]^-$ and $\sim 98\%$ for $[\text{PtCl}_4]^{2-}$. It would therefore be safe to argue that the observed photocatalytic reduction trend is as a direct result of these dominant species. From Fig. 2 it is also clear that at the chloride concentration where the $[\text{PtCl}_4]^{2-}$ -complex predominates, Pt(II) does not reduce and stays in solution. At the other chloride concentrations photocatalytic reduction does occur

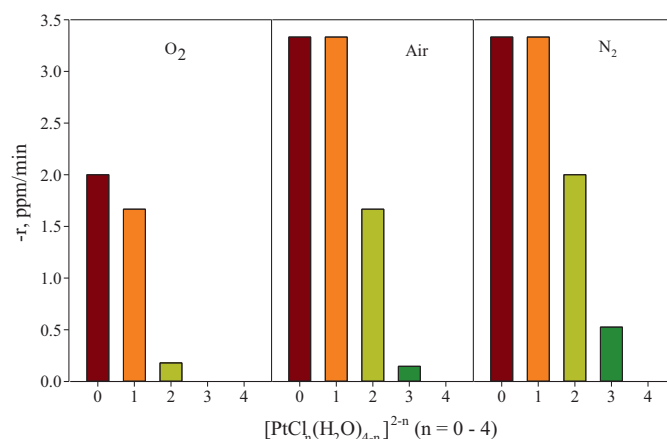


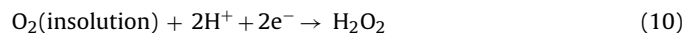
Fig. 3. Initial rates for the photocatalytic reduction of the $[\text{PtCl}_n(\text{H}_2\text{O})_{4-n}]^{2-n}$ system ($n=0-4$) in three atmospheres.

to a greater or lesser extent depending on the composition of the solution.

The observed photocatalytic reduction rate trends (in air-equilibrated and oxygen saturated solutions) have indeed shown that at the Cl^- -concentration where $[\text{PtCl}_4]^{2-}$ predominates, Pt(II) is resisting reduction whereas the other complexes are in fact reduced (Figs 2 and 3). As no sacrificial reducing agent has been added to the system, the only expected source of electrons has to be H_2O . It has been reported earlier [5], with dissolved oxygen having a solubility of only 8.5 ppm in aqueous solutions, it is expected that this will not have any negative impact on the photocatalytic reduction of the Pt(II)-species. Having a standard reduction potential of 1.229 V (Eq. (9)), it is expected that all the initial dissolved oxygen will be reduced first and removed from solution followed by the photocatalytic reduction of the Pt(II)-species. The photocatalytic reduction of the Pt(II)-species necessitates that electrons are fed to the positive holes in the valence bands of the semiconductor. The only source of electrons in this system is water and its oxidation results in the reintroduction of oxygen into the system. This photocatalytically generated oxygen will then be reduced and removed, followed again by the photocatalytic reduction of the Pt(II)-species. At low pH values and high concentration of chlorides, hydrolysis is negligible [7] and in this case it is not the explanation for the inability of $[\text{PtCl}_4]^{2-}$ to reduce. One of the reasons given [7,22] for this at low pH and high concentration of chlorides is that the oxygen produced during bulk water decomposition remains adsorbed on the TiO_2 surface and is reduced by electron trapping. This process is competitive to platinum reduction, since it is also trapping electrons. From this analysis it is therefore clear that it is not only bulk water that acts as an SRA but also water in the coordination sphere with the chlorides of Pt(II) that is necessary for measurable photocatalytic reduction to take place.

In photocatalytic reduction systems, dissolved oxygen from air has been shown to significantly influence the photocatalytic reduction rate of some metal ions on Evonik-Degussa P25 photocatalyst [17]. Oxygen was found to be detrimental to the photocatalytic reduction of rhodium(III) and interfered in the photocatalytic reduction of platinum(IV) and palladium(II), particularly in acidic media where reduction of O_2 is a more thermodynamically favourable process [23]. In addition, oxygen can be produced from water (acting as SRA), but its stoichiometric quantity is not always detected because of its adsorption on the surface of the TiO_2 particles. Therefore, one can expect that in the absence of dissolved oxygen, by purging the solution with nitrogen, a higher photocatalytic reduction rate of Pt(II) ions might be achieved. In order to investigate this influence, experiments were carried out in nitrogen

purged solutions. The effect of saturating the solution with pure nitrogen is also shown in Figs. 2 and 3, where it is obvious that the absence of oxygen enhances the reduction of those complexes that have H₂O in their coordination spheres. Comparing the initial photocatalytic reduction rates in Fig. 3, it is clear that oxygen is detrimental to the photocatalytic reduction of water containing chloro Pt(II) complexes. It is important to note that since the minimum sampling time was 15 min, it is possible that the photocatalytic reduction rate of some of the complexes is quite fast and the reaction goes to completion before sampling. It is known that the amount of oxygen in solution decreases with increasing irradiation time, due to its reduction by the photogenerated electrons to give hydrogen peroxide according to Eq. (10) [24].



Under a nitrogen-atmosphere, no H₂O₂ formation was detected in earlier works [20] suggesting that H₂O₂ is produced from the oxygen reduction reaction (10) and not from water oxidation as shown in Eq (11).



This result was found to be consistent with the fact that the quantity of H₂O₂ produced under illumination decreased on lowering the O₂ pressure [25] and it was concluded that O₂ competed with Cr(VI) for the photogenerated electrons in the semiconductor. Thus, one can expect that in the absence of O₂ in solution, by purging with N₂, a large amount of Pt(II) might be photocatalytically reduced. This was found to hold true for those complexes that have water molecules in their coordination spheres compared to the inability of [PtCl₄]²⁻ to reduce (Fig. 2).

TiO₂ is generally regarded as an n-type semiconductor, due to intrinsic oxygen deficiencies, resulting in the Fermi level being more or less close to the conduction band or flat band potential. Upon ultraviolet light irradiation the Fermi level splits into two quasi-Fermi levels, one for the electron, E_{F}^{n} and one for the positive hole, E_{F}^{p} , with E_{F}^{n} practically merging with the conduction band or flat band potential [26]. At pH = 1, employed in this study, the flat band potential of Evonik–Degussa P25 is –0.36 V and should allow for the reduction of all Pt(II)–chloride species. This is however not the case as [PtCl₄]²⁻ is not reduced, which highlights the fact that thermodynamics is not the only parameter affecting the photocatalytic reduction of the [PtCl_n(H₂O)_{4–n}]^{2–n} (n = 0–4) system, and that surface processes play a significant part similar to the case reported in our earlier communication [5].

3.3. Comparison of photocatalytic reduction trends of Pt(II) and Pd(II) chloro aqua complexes within 15 min of illumination in air

In an earlier study we reported on the photocatalytic reduction of the [PdCl_n(H₂O)_{4–n}]^{2–n} (n = 0–4) system in the absence of an added sacrificial reducing agent [5]. Fig. 4 serves to highlight the difference between Pt(II) and Pd(II) by depicting the amount of Pt(II) and Pd(II) that is photocatalytically reduced, as part of the [PtCl_n(H₂O)_{4–n}]^{2–n} (n = 0–4) and [PdCl_n(H₂O)_{4–n}]^{2–n} (n = 0–4) systems, within the first 15 min of illumination. It is clearly seen how [Pd(H₂O)₄]²⁺ (n = 0) and [PdCl(H₂O)₃]⁺ (n = 1) drop off from the expected photocatalytic reduction rate trend as predicted by the increase in standard reduction potentials of the complexes from n = 4 to n = 0. An increase in the amount of coordinated H₂O's would seem to be working against an expected photocatalytic reduction rate increase as predicted by an increase of the standard reduction potentials of the [PdCl_n(H₂O)_{4–n}]^{2–n} (n = 0–4) system (see Ref. [5] for a detailed explanation). On the other hand the photocatalytic reduction of Pt(II) complexes (Fig. 4) follows the thermodynamic trend shown by Eqs. (4)–(8) despite an increase in the number of coordinated H₂O's, and it would therefore seem that oxidation of

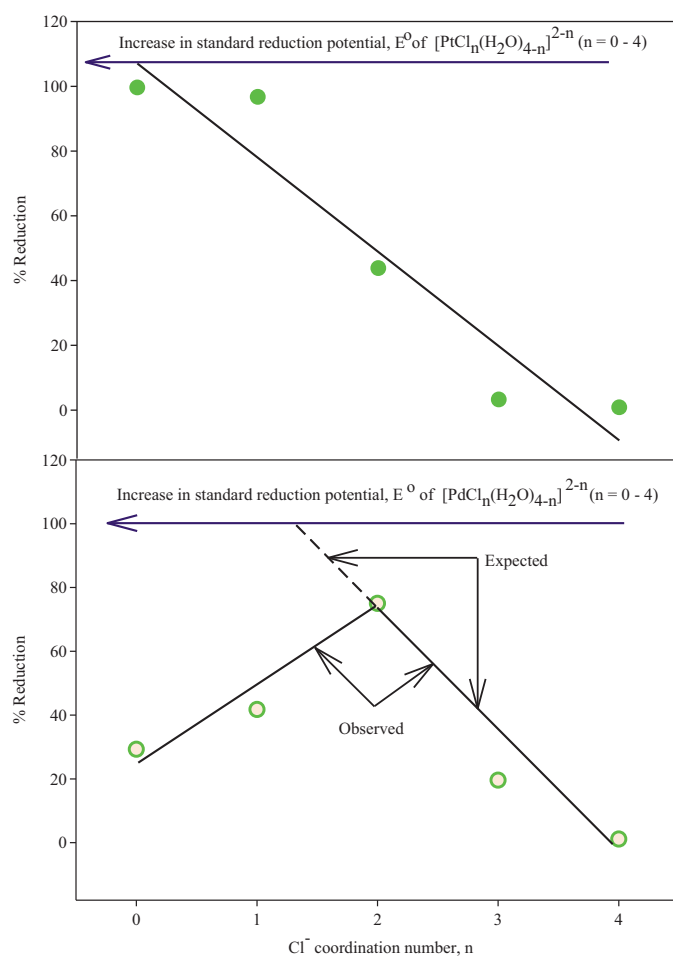
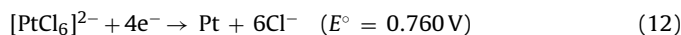


Fig. 4. Observed photocatalytic reduction rate trends Pt(II) and Pd(II) chloro aqua complexes within 15 min of illumination (see also Ref. [5]).

coordinated H₂O's in the case of Pt(II) either does not come into play or does not have a negative effect on the overall photocatalytic reduction. In general, however, the standard reduction potential values, for the corresponding complexes, are higher for Pt(II) than Pd(II). This photocatalytic reduction 'discrepancy' between Pt(II) and Pd(II) might point towards differences in complex–catalyst interaction where [Pt(H₂O)₄]²⁺ (n = 0) and [PtCl(H₂O)₃]⁺ (n = 1) are nearly 100% reduced, after only 15 min, as compared to only 30–40% for [Pd(H₂O)₄]²⁺ (n = 0) and [PdCl(H₂O)₃]⁺ (n = 1) despite having favourable standard reduction potentials. A mechanistic study was not conducted and to that regard it is unclear why a change in reaction rate trend is observed for Pt(II) and Pd(II).

3.4. Photocatalytic reduction of Pt(IV) from K₂PtCl₆ and H₂PtCl₆

The photocatalytic reduction of Pt(IV) from [PtCl₆]²⁻, in three different atmospheres namely air, pure oxygen and nitrogen, was carried out for comparison purposes against the photocatalytic reduction of Pt(II) from [PtCl₃(H₂O)]⁻ since they have comparable reduction potentials (Eqs. (7) and (12)) and [PtCl₄]²⁻ since it has maximum number of chloride ions around the central Pt ion just like [PtCl₆]²⁻. The reduction reaction of [PtCl₆]²⁻ can be written as follows [10,27]:



Eq. (12) shows that the reduction of Pt(IV) to Pt⁰ is thermodynamically feasible since the reduction potential is more positive than the flat-band potential of anatase TiO₂ which is –0.36 V at pH 1. Fig. 5

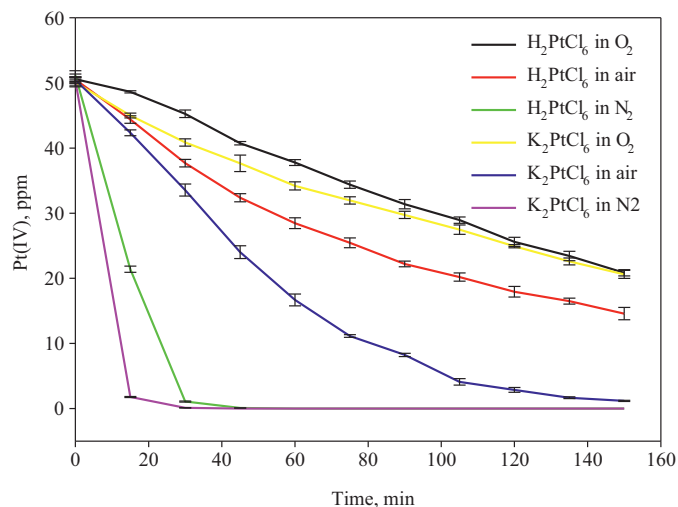


Fig. 5. Photocatalytic reduction trends of K_2PtCl_6 and H_2PtCl_6 in the absence of an added SRA in air, oxygen and nitrogen.

shows the photocatalytic reduction of the two Pt(IV) compounds in air, oxygen and nitrogen saturated solutions where the kinetics of reduction confirms that the reaction mechanism depends on the nature of the Pt(IV) precursors [10].

The photocatalytic recovery of platinum from $PtCl_6^{2-}$ ions in an aqueous suspension of anatase TiO_2 in conditions resembling a hydrometallurgical practice (low Pt concentration, low pH and high Cl^-) has been described in literature [7]. In those standard conditions it was observed that no photoreaction took place without methanol as an SRA. In that work, at low pH and high chloride concentration hydrolysis was assumed negligible and thus could not be the reason for the lack of photocatalytic reduction. In other investigations on the photocatalytic recovery of platinum metal Pt^0 from Pt(IV) solutions, contradicting conclusions were made. For example, in references [10,11,23] photocatalytic reduction of Pt(IV) to Pt^0 was successfully carried out without an added organic SRA but in reference [28] it is stated that a product of $[PtCl_6]^{2-}$ hydrolysis (the hydrosylate) is the one that is photocatalytically converted into a solid deposit presumably by reduction. From these sources, Table 4, showing the concentrations of the Pt(IV) precursors subjected to photocatalytic reduction from different investigators was compiled and subjected to close scrutiny as it is particularly important to note the differences of the chloride concentrations reported in literature. Identification of the photodeposits from the photocatalytic reduction of Pt(II and IV) chloro complexes through techniques such as TEM and XPS is a subject of our future investigations.

In Table 4 it is clear that the highest amount of chloride was used in references [7,28] where photocatalytic reduction of $[PtCl_6]^{2-}$ was not observed in the absence of an organic SRA. The authors [28], gave details on the relationship between hydrolysis

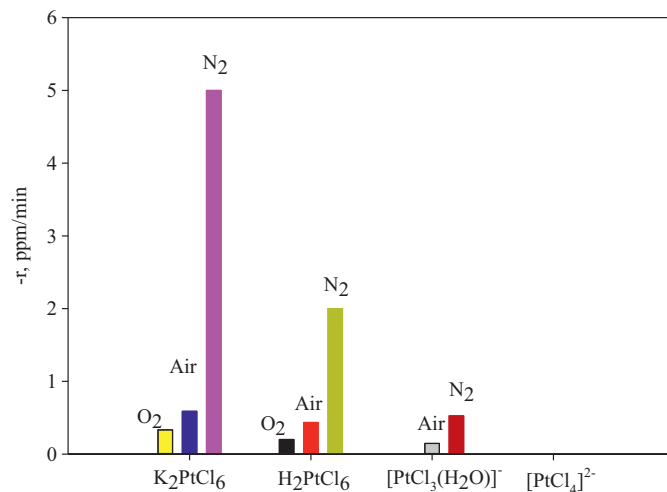


Fig. 6. Initial rates for the photocatalytic reduction of the highly chlorinated Pt(II) and Pt(IV) complexes in three atmospheres.

of $[PtCl_6]^{2-}$ and photocatalytic reduction where it was proven that upon UV illumination the former reaction is accelerated. They went further to observe that the extent of $[PtCl_6]^{2-}$ hydrolysis varies with the H^+ and Cl^- concentration and when the concentration of these ions is sufficiently high it inhibits the hydrolysis of the $[PtCl_6]^{2-}$ ion and no photodeposit is observed on the TiO_2 surface. In our study, however, some photodeposit was visibly observed probably due to the low concentration of the chloride and high concentration of H^+ from $HClO_4$ (pH = 1). Comparing the photocatalytic reduction trends (Figs. 2 and 5) of $[PtCl_3(H_2O)]^-$ ($E^\circ = 0.769$ V), $[PtCl_6]^{2-}$ ($E^\circ = 0.760$ V) and $[PtCl_4]^{2-}$ ($E^\circ = 0.710$ V) in all the three atmospheres one sees that the first two have comparable standard reduction potentials meaning that they should have a similar reduction pattern. The chloride concentration in the two complexes was 4.06×10^{-3} M for $[PtCl_3(H_2O)]^-$ (according to speciation) which is slightly higher than 1.54×10^{-3} M for $[PtCl_6]^{2-}$. If one looks at the initial rates for the photocatalytic reduction of these complexes (Fig. 6), it is clear that $[PtCl_6]^{2-}$ reduces faster than $[PtCl_3(H_2O)]^-$ in all the three atmospheres and $[PtCl_4]^{2-}$ with a chloride concentration of 8.89×10^{-1} M from speciation data does not reduce at all. The higher chloride concentration as well as the low standard reduction potential compared to the other two complexes is evidence enough that $[PtCl_4]^{2-}$ would be more difficult to reduce. This observation also leads to the conclusion that, despite the maximum chloride ions in the coordination sphere for $[PtCl_4]^{2-}$ and $[PtCl_6]^{2-}$, the mechanism of photocatalytic reduction for the two complexes is different. Since the chloride concentration was lower in the $[PtCl_6]^{2-}$ complex, hydrolysis could have taken place leading to a mixture of chloro hydroxo platinum(IV) complexes [29]. These complexes have an OH^- group

Table 4
Pt(IV) precursors subjected to photocatalytic reductions from various researchers in acidic conditions.

Source	Concentration (mol l ⁻¹)					
	K_2PtCl_6		H_2PtCl_6		Na_2PtCl_6	
	Pt^{IV}	Cl^-	Pt^{IV}	Cl^-	Pt^{IV}	Cl^-
This study	2.56×10^{-4}	1.54×10^{-3}	2.56×10^{-4}	1.54×10^{-3}	–	–
Ref. [7]	–	–	2.56×10^{-4}	4.07×10^{-2}	–	–
Ref. [10]	–	–	10^{-3}	6×10^{-3}	10^{-3}	6×10^{-3}
Ref. [11]	–	–	–	–	2×10^{-3}	1.2×10^{-2}
Ref. [23]	–	–	6.40×10^{-4}	3.84×10^{-3}	–	–
Ref. [28]	–	–	7.70×10^{-2}	4.62×10^{-1}	–	–

–, not reported.

in their coordination sphere, which can act as an SRA speeding up the photocatalytic reduction process (compare with Ref. [5]). An attempt to identify these complexes was not carried out at this time and the reaction solution ageing before photocatalytic reduction in the absence of an added organic SRA was not probed. Similarly, no attempts were made to identify the exact nature of the photo deposited species using various characterization techniques as it was beyond the scope of this communication.

3.5. Adsorption (dark test) and photolysis of $[\text{Pt}(\text{H}_2\text{O})_4]^{2+}$ and K_2PtCl_6

From the photocatalytic tests it was noticed that $[\text{Pt}(\text{H}_2\text{O})_4]^{2+}$ and K_2PtCl_6 were the fastest reducing complexes at pH 1 and thus blank runs under similar experimental conditions were undertaken to ascertain whether the depletion of platinum from solution was indeed a photocatalytic reduction process and if other processes could be involved. For this both complexes were subjected to 150 min runs in the absence of either UV illumination (TiO_2 only) or TiO_2 (UV illumination only). Both complexes did not reduce at all which means that the driving force for the photocatalytic reduction process was therefore the combined effect of UV light and TiO_2 .

4. Conclusion

For the photocatalytic reduction of chloro aqua complexes of platinum(II) as a means of metal recovery from solution in the absence of an added organic sacrificial reducing agent (SRA), the presence of coordinated water molecules determine the rate of reaction. An inert atmosphere enhances the photocatalytic reduction of those platinum(II) chloro complexes with water molecules in their coordination sphere. Oxygen is detrimental for the photocatalytic reduction of the chloro aqua platinum(II) ions. The thermodynamics of reduction shown by the redox potential of the complexes was a good prediction of the trend of photocatalytic reduction of the chloro aqua complexes of platinum(II) unlike the case with chloro aqua complexes of palladium(II). The mechanism for the photocatalytic reduction of the chloro platinum(IV) complex is different from that of the chloro platinum(II) complex in the absence of an added organic SRA. It is therefore postulated that the photocatalytic reduction of $[\text{PtCl}_6]^{2-}$ proceeds through chloro hydroxo platinum(IV) complexes such as $[\text{Pt}(\text{OH})\text{Cl}_5]^{2-}$.

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